Supplementary Material

PhI(OAc)$_2$-BF$_3$-OEt$_2$ Mediated Domino Imine Activation, Intramolecular C-C Bond Formation and β-Elimination: New Approach for the synthesis of Fluorenones, Xanthones and Phenanthridines†

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General information

All reagents were purchased from commercial suppliers and used without further purification. IR spectra of the compounds were recorded on Perkin-Elmer AC-1 spectrometer. $^1$H NMR spectra were run on Bruker Advance DPX 300 MHz spectrometer in CDCl$_3$ and TMS was used as internal standard. ESI mass spectra were recorded on JEOL SX 102/DA-6000. Silica gel 60-120 and 230-400 mesh was used as stationary phase to isolate the compounds. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) was distilled over calcium hydride. Aldimines (2, 12-19, 29, 32, 37-39 and 46-48) were prepared from condensation of the corresponding aldehydes with amines according to the literature method.†
Structures of Aldimines (2, 12-19, 29, 32, 37-39 and 46-48)
General procedure (I) for synthesis of biaryl-2-carbaldehydes

5 mmol of 2-bromobenzaldehyde, 6 mmol of arylboronic acid and 0.5 mmol of Pd(PPh$_3$)$_4$ were taken in a round bottom flask. 10 ml of DMF was added in the reaction mixture and stirred for 2 min. 10 ml of 2(M) Na$_2$CO$_3$ solution was then added and then refluxed for 4-8 h at 80 °C. The reaction mixture was extracted with ethyl acetate (2 x 10 mL). The combined ethyl acetate layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum to yield the crude product, which was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

Spectroscopic data of biaryl-2-carbaldehydes

2-(naphthalen-2-yl)benzaldehyde (1): Following the general procedure (I), 1 was prepared from naphthalen-2-ylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil 373 mg (59% yield); IR (KBr): $\nu$ max 3058, 3020, 2860, 1695 cm$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 10.08 (s, 1H), 8.11 (d, $J = 7.7$ Hz, 1H), 7.98-7.85 (m, 4H), 7.72-7.60 (m, 1H), 7.58-7.56 (m, 5H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 192.4 (C), 145.9 (C), 135.2 (C), 134.0 (C), 133.6 (CH), 133.0 (C), 132.8 (C), 131.0 (CH), 129.5 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH); MS (ESI): $m/z$ = 233.1 (M+H)$^+$. The compound was previously reported by Larock et al.$^2$

3',4'-dichlorobiphenyl-2-carbaldehyde (4): Following the general procedure (I), 4 was prepared from 3,4-dichlorobenzaldehyde and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Yellow solid 412 mg (61% yield); m.p. 136-138 °C; IR (KBr): 3035, 2850, 1692, 777, 766 cm$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 10.15 (s, 1H), 7.94 (dd, $J = 7.3$, 1.4 Hz, 1H), 7.77 (dd, $J = 7.5$, 1.6 Hz, 1H), 7.72-7.63 (m, 3H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.31 (dd, $J = 7.4$, 1.3 Hz, 1H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 193.2 (C), 139.3 (C), 137.4 (C), 137.4 (C), 135.0 (CH), 134.2 (C), 131.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 127.0 (CH), 126.3 (CH), 126.1 (CH); MS (ESI): $m/z$ = 251.1 (M+H)$^+$. The compound was previously reported.$^2$

4'-chlorobiphenyl-2-carbaldehyde (5): Following the general procedure (I), 5 was prepared from 4-chlorobenzaldehyde and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 383 mg (67% yield). Spectroscopic data was identical with that previously reported.$^3$

4'-methylbiphenyl-2-carbaldehyde (6): Following the general procedure (I), 6 was prepared from 4-methylbenzaldehyde and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 382 mg (72% yield). Spectroscopic data was identical with that previously reported.$^4$
4'-ethylbiphenyl-2-carbaldehyde (7): Following the general procedure (I), 7 was prepared from 4-ethylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 407 mg (68% yield); IR (Neat): 3020, 2965, 2930, 2845, 1698 cm\(^{-1}\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.03 (s, 1H), 8.04 (d, \(J = 6.9\) Hz, 1H), 7.68-7.62 (m, 1H), 7.52-7.46 (m, 2H), 7.33 (brs, 4H), 2.74 (q, \(J = 7.6\) Hz, 2H), 1.33 (t, \(J = 7.6\) Hz, 3H); \(^1\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 192.6 (C), 146.0 (C), 135.0 (C), 133.8 (C), 133.5 (CH), 130.8 (CH), 130.1 (2CH), 127.9 (2CH), 127.5 (CH), 28.6 (CH\(_2\)), 15.5 (CH\(_3\)); MS (ESI): \(m/z\) 211.1 (M+H)

4'-propylbiphenyl-2-carbaldehyde (8): Following the general procedure (I), 8 was prepared from 4-propylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 450 mg (74% yield); IR (Neat): 3032, 2945, 2862, 1696 cm\(^{-1}\); MS (ESI): \(m/z\) 225.1 (M+H); \(^1\)H- and \(^13\)C-NMR data was identical with that previously reported.\(^5\)

4'-isopropylbiphenyl-2-carbaldehyde (9): Following the general procedure (I), 9 was prepared from 4-isopropylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 405 mg (68% yield). Spectroscopic data was identical with that previously reported.\(^6\)

4'-tert-butylbiphenyl-2-carbaldehyde (10): Following the general procedure (I), 10 was prepared from 4-tertbutylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 445 mg (69% yield). Spectroscopic data was identical with that previously reported.\(^7\)

Biphenyl-2-carbaldehyde (11): Following the general procedure (I), 11 was prepared from phenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 344 mg (69% yield). Spectroscopic data was identical with that previously reported.\(^8\)
2-(benzofuran-3-yl)benzaldehyde (28): Following the general procedure (I), 28 was prepared from benzofuran-3-ylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 85 : 15). Pale yellow oil 410 mg (68% yield). Spectroscopic data was identical with that previously reported.2

2-(naphthalen-1-yl)benzaldehyde (31): Following the general procedure (I), 31 was prepared from naphthalen-1-ylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). White solid 362 mg (58% yield); m.p.: 88-90°C (lit m.p. 87-88°C). Spectroscopic data was identical with that previously reported.10

General procedure (II) for synthesis of the 2-(aryloxy)benzaldehydes11

To a solution of DMA (10 mL) containing 2-fluorobenzaldehyde (5.0 mmol) and hydroxy benzene derivative (5.0 mmol), was added K2CO3 (5.0 mmol) and the reaction mixture was stirred for 2 h at 170°C under an Argon atmosphere. It was then cooled to room temperature and after usual workup and concentration, crude mixture was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

Spectroscopic data of 2-(aryloxy)benzaldehydes

2-(p-tolyloxy)benzaldehyde (34): Following the general procedure (II), 34 was prepared from 4-methylphenol and 2-fluorobenzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 512 mg (60% yield). Spectroscopic data was identical with that previously reported.12

2-(4-tert-butylphenoxy)benzaldehyde (35): Following the general procedure (II), 35 was prepared from 4-tertbutylphenol and 2-fluorobenzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 650 mg (65% yield). Spectroscopic data was identical with that previously reported.2

2-phenoxybenzaldehyde (36): Following the general procedure (II), 36 was prepared from phenol and 2-fluoro benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 496 mg (62% yield). Spectroscopic data was identical with that previously reported.13

General procedure (III) for synthesis of biaryl-2-amines14

To a 100 mL round bottom flask, aryl boronic acid (3.0 mmol), K2CO3 (8.0 mmol), and Pd(PPh3)4 (0.2 mmol) were dissolved in 15 mL of toluene followed by the addition of 3 mL of H2O and 5 mL of EtOH. 2-Bromoaniline (2.0 mmol) was then added and the resulting mixture was heated at 100°C for 16 h. After cooling to room temperature, the reaction mixture was diluted...
with 30 mL of saturated aqueous NH₄Cl and 30 mL of CH₂Cl₂. The aqueous phase was extracted with an additional 2 × 30 mL of CH₂Cl₂, and the combined organic layers were washed with 30 mL of water and 30 mL of saturated aqueous NaHCO₃. The organic phase was dried over Na₂SO₄ and filtered. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

**Spectroscopic data of biaryl-2-amines**

![Biaryl-2-amine](image)

4'-chlorobiphenyl-2-amine (43): Following the general procedure (III), 43 was prepared from 4-chlorophenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Yellow oil 15 410 mg (69% yield). Spectroscopic data was identical with that previously reported. 15

![Biaryl-2-amine](image)

4'-methylbiphenyl-2-amine (44): Following the general procedure (III), 44 was prepared from 4-methylphenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Brown oil 16 332 mg (62% yield). Spectroscopic data was identical with that previously reported. 16

![Biaryl-2-amine](image)

biphenyl-2-amine (45): Following the general procedure (III), 45 was prepared from phenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Brown solid 17 310 mg (63% yield). mp. 51-54 °C (lit. 17 m.p. 52-54 °C); Spectroscopic data was identical with that previously reported. 17

**General procedure (IV) for synthesis of fluorenones, anthranone and xanthones**

Aldimine (0.25 mmol) was dissolved in DCE (1.0 ml) and added in mixture of PhI(OAc)₂ (0.375 mmol) and BF₃-OEt₂ (0.375 mmol) in DCE (3 ml). The resulting reaction mixture was stirred at room temperature for 5 min and then was refluxed for 24-30 h at 80 °C and then cooled to room temperature. 1N HCl (2 ml) was added and stirred for 2-6 h at room temperature. Diluted with H₂O and extracted with diethyl ether (2 x 15 mL). The organic layers were combined, dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure to afford the residue, which was purified by column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexane as the eluent to provide the desired product.

**Spectroscopic data of fluorenones, anthranone and xanthones**

![Fluorenone](image)

1H-benzo[b]fluoren-11-one (3): Following the general procedure (IV), 3 was prepared from aldimine 2 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid 18 (60 mg, 61% yield); m.p.: 142-144 °C (lit. 18 m.p. 141-142 °C); IR (KBr); v max 3042, 1710, 1604, 895 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 8.17 (s, 1H), 7.89-7.86 (m, 2H), 7.85 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.57-7.53 (m, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ 193.1 (C), 144.8 (C), 138.5 (C), 136.9 (C), 136.2
(C), 135.0 (CH), 133.9 (C), 132.7 (C), 130.8 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 126.6 (CH), 125.6 (CH), 124.4 (CH), 120.8 (CH), 119.0 (CH); MS (ESI): \( m/z = 231.1 \) (M+H)+; HRMS (ESI) calculated for \( C_{17}H_{10}O: 230.0732 \), found: 231.0734 (M+H)+. Spectroscopic data was compared with that previously reported.\(^{18}\)

2,3-dichloro-9H-fluoren-9-one (20): Following the general procedure (IV), 20 was prepared from aldimine \( 12 \) and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 85 : 15). Yellow solid (64 mg, 65% yield); m.p.: 134-136 °C; IR (KBr): \( \nu_{\text{max}} 1712, 1602, 777 \text{ cm}^{-1} \); \( ^{1}H\)-NMR (300 MHz, CDCl\( _3 \)): \( \delta 7.75 (s, 1H), 7.61 (s, 1H), 7.57 (dd, J = 7.8, 1.5 \text{ Hz}, 1H), 7.49 (dd, J = 7.5, 1.4 \text{ Hz}, 1H), 7.43-7.37 (m, 1H), 7.31-7.25 (m, 1H); \( ^{13}C\)-NMR (75 MHz, CDCl\( _3 \)): \( \delta 195.9 \) (C), 143.8 (C), 142.5 (C), 140.4 (C), 136.9 (C), 136.1 (C), 135.7 (C), 133.9 (C), 129.5 (CH), 128.3 (CH), 125.8 (CH), 123.0 (CH), 122.2 (CH); MS (ESI): \( m/z = 249.1 \) (M+H)+; HRMS (ESI) calculated for \( C_{13}H_{6}Cl_2O: 247.9796 \), found: 248.9798 (M+H)+.

2-chloro-9H-fluoren-9-one (21): Following the general procedure (IV), 21 was prepared aldimine \( 13 \) and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow solid \( 58 \) mg (59% yield). m.p.: 120-121 °C (lit.\(^{19}\) mp 118-120 °C); Spectroscopic data was identical with that previously reported.\(^{19}\)

2-methyl-9H-fluoren-9-one (22): Following the general procedure (IV), 22 was prepared from aldimine \( 14 \) and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid \( 56 \) mg (57% yield). m.p.: 92-94 °C (lit.\(^{19}\) mp 92 °C); Spectroscopic data was identical with that previously reported.\(^{19}\)

2-ethyl-9H-fluoren-9-one (23): Following the general procedure (IV), 23 was prepared from aldimine \( 15 \) and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 56 mg (57% yield); IR (Neat): 1720, 1600, 1450 cm\(^{-1}\); \( ^{1}H\)-NMR (300 MHz, CDCl\( _3 \)): \( \delta 7.64-7.58 (m, 2H), 7.50-7.41 (m, 3H), 7.30-7.22 (m, 2H), 2.72 (q, J = 6.8 \text{ Hz}, 2H), 1.30 (t, J=6.6 \text{ Hz}, 3H); \( ^{13}C\)-NMR (75 MHz, CDCl\( _3 \)): \( \delta 194.2 \) (C), 144.9 (C), 141.2 (C), 139.8 (C), 135.9 (C), 135.4 (C), 134.7 (CH), 134.5 (CH), 128.5 (CH), 125.7 (CH), 125.2 (CH), 121.5 (CH), 121.1 (CH), 28.7 (CH\( _2 \)), 13.0 (CH\( _3 \)); MS (ESI): \( m/z = 209.1 \) (M+H)+; HRMS (ESI) calculated for \( C_{15}H_{12}O: 208.0888 \), found: 209.0887 (M+H)+.

2-propyl-9H-fluoren-9-one (24): Following the general procedure (IV), 24 was prepared from aldimine \( 16 \) and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil 54 mg (55% yield); IR (Neat): 2935, 1722, 1605, 1480, 1450 cm\(^{-1}\); \( ^{1}H\)-NMR (300 MHz, CDCl\( _3 \)): \( \delta 7.65 (d, J = 1.3 \text{ Hz}, 1H), 7.58 (dd, J = 7.3, 1.5 \text{ Hz}, 1H), \ldots\)
1H), 7.51-7.46 (m, 2H), 7.31-7.26 (m, 1H), 2.54 (t, J = 7.4 Hz, 2H), 1.78-1.67 (m, 2H), 1.05 (t, J = 6.5 Hz, 2H); 13C-NMR (75 MHz, CDCl3): δ 194.4 (C), 144.1 (C), 141.4 (C), 139.2 (C), 135.6 (C), 134.8 (C), 134.2 (CH), 133.6 (CH), 128.8 (CH), 128.3 (CH), 125.8 (CH), 121.8 (CH), 121.4 (CH), 38.6 (CH3), 24.5 (CH2), 13.0 (CH3); MS (ESI): m/z = 223.1 (M+H)+; HRMS (ESI) calculated for C16H14O: 222.1045, found: 223.1044 (M+H)+.

2-isopropyl-9H-fluoren-9-one (25): Following the general procedure (IV), 25 was prepared from aldimine 17 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil (57 mg, 58% yield); IR (Neat): 1710, 1612, 1380 cm⁻¹; 1H-NMR (300 MHz, CDCl3): δ 7.67 (d, J = 1.3 Hz, 1H), 7.63 (dd, J = 7.4, 1.3 Hz, 1H), 7.51-7.47 (m, 3H), 7.38 (dd, J = 7.4, 1.3 Hz, 1H), 7.31-7.25 (m, 1H), 3.23-3.11 (m, 1H), 1.33 (d, J = 6.4 Hz, 6H); 13C-NMR (75 MHz, CDCl3): δ 194.2 (C), 144.9 (C), 143.2 (C), 141.6 (C), 139.1 (C), 135.4 (C), 134.5 (CH), 130.3 (CH), 127.5 (CH), 125.1 (CH), 121.9 (CH), 121.1 (CH), 119.1 (CH), 34.3 (C), 23.2 (2CH3); MS (ESI): m/z = 223.1 (M+H)+; HRMS (ESI) calculated for C16H14O: 222.1045, found: 223.1042 (M+H)+.

2-tert-butyl-9H-fluoren-9-one (26): Following the general procedure (IV), 26 was prepared from aldimine 18 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil (54 mg, 55% yield); IR (Neat): 1712, 1595, 1385 cm⁻¹; 1H-NMR (300 MHz, CDCl3): δ 7.66 (d, J = 1.4 Hz, 1H), 7.59 (dd, J = 7.5, 1.4 Hz, 1H), 7.47-7.33 (m, 4H), 7.27-7.22 (m, 1H), 1.35 (s, 9H); 13C-NMR (75 MHz, CDCl3): δ 194.3 (C), 151.9 (C), 144.3 (C), 141.7 (C), 138.4 (C), 135.5 (C), 134.6 (CH), 130.9 (CH), 128.7 (CH), 125.2 (CH), 122.9 (CH), 121.3 (CH), 119.9 (CH), 35.0 (C), 31.4 (3CH3); MS (ESI): m/z = 237.1 (M+H)+; HRMS (ESI) calculated for C17H16O: 236.1201, found: 237.1211 (M+H)+.

9H-fluoren-9-one (27): Following the general procedure (IV), 27 was prepared from aldimine 19 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid (46 mg, 47% yield). m.p.: 82-85 °C (lit.20 mp 82-83 °C); Spectroscopic data was identical with that previously reported.20

6H-benzo[d]indeno[2,1-b]furan-6-one (30): Following the general procedure (IV), 30 was prepared from aldimine 29 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Orange yellow solid (42 mg, 66% yield); m.p.: 110-112 °C (lit.21 m.p. 109-110 °C); IR (KBr): νmax 3025, 1720 cm⁻¹; 1H NMR (300 MHz, CDCl3): δ 7.72 (dd, J = 7.9, 0.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.61-7.47 (m, 1H), 7.45-7.17 (m, 4H); 13C NMR (75 MHz, CDCl3): δ 179.6 (C), 163.2 (C), 155.9 (C), 144.9 (C), 141.0 (C), 135.3 (C), 135.2 (CH), 128.4 (CH), 127.9 (C), 121.8 (CH), 120.8 (CH), 120.1 (CH), 116.8 (CH), 112.6 (CH); MS (ESI): m/z = 221.2 (M+H)+; HRMS (ESI) calculated for C15H13O2: 220.0524, found: 221.0525 (M+H)+. Spectroscopic data was compared with that previously reported.21
7H-benzo[de]anthracen-7-one (33): Following the general procedure (IV), 33 was prepared from aldimine 31 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid\(^\text{18}\) (44 mg, 68% yield); m.p.: 160-162 °C (lit.\(^\text{18}\) m.p. 162-166 °C); IR (KBr): \(\nu_{\text{max}}\) 3040, 1650, 1597 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.77 (d, \(J = 7.6\) Hz, 1H), 8.52 (d, \(J = 7.2\) Hz, 1H), 8.45 (d, \(J = 7.2\) Hz, 1H), 8.32 (d, \(J = 8.0\) Hz, 1H), 8.22 (d, \(J = 8.0\) Hz, 1H), 8.00 (d, \(J = 8.0\) Hz, 1H), 7.88-7.72 (m, 2H), 7.69 (t, \(J = 8.0\) Hz, 1H), 7.54 (t, \(J = 7.7\) Hz, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 183.8 (C), 136.1 (C), 135.1 (CH), 133.5 (CH), 133.0 (C), 131.3 (C), 130.2 (CH), 129.7 (CH), 128.5 (C), 128.2 (CH), 128.1 (CH), 127.9 (C), 126.8 (C), 126.5 (CH), 126.5 (CH), 124.1 (CH), 123.0 (CH); MS (ESI): \(m/z\) = 231.1 (M+H\(^+\)). Spectroscopic data was compared with that previously reported.\(^\text{18}\)

2-methyl-9H-xanthen-9-one (40): Following the general procedure (IV), 40 was prepared from aldimine 37 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil (76 mg, 74% yield). IR (KBr): \(\nu_{\text{max}}\) 3060, 2920, 2864, 1658 cm\(^{-1}\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.27 (dd, \(J = 7.8, 1.6\) Hz, 1H), 8.05 (s, 1H), 7.72-7.67 (m, 1H), 7.49-7.38 (m, 3H), 7.33 (d, \(J = 7.5\) Hz, 1H), 2.41 (s, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 177.3 (C), 156.4 (C), 154.3 (C), 147.6 (C), 134.8 (CH), 133.4 (CH), 126.1 (CH), 125.7 (CH), 123.5 (CH), 121.9 (C), 119.2 (C), 118.7 (CH), 118.3 (CH), 20.8 (CH\(_3\)); MS (ESI): \(m/z\) = 211.1 (M+H\(^+\)). Spectroscopic data was compared with that previously reported.\(^\text{2}\)

2-tert-butyl-9H-xanthen-9-one (41): Following the general procedure (IV), 35 was prepared from aldimine 38 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil (67 mg, 68% yield); IR (Neat): \(\nu_{\text{max}}\) 2965, 2867, 1661 cm\(^{-1}\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.32-8.28 (m, 2H), 7.77 (dd, \(J = 8.8, 2.5\) Hz, 1H), 7.72-7.67 (m, 1H), 7.49-7.43 (m, 2H), 3.17-3.36 (m, 1H), 1.40 (s, 9H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 177.4 (C), 156.5 (C), 154.9 (C), 147.6 (C), 134.8 (CH), 133.5 (CH), 127.4 (CH), 123.7 (CH), 122.7 (CH), 122.0 (C), 121.3 (C), 119.2 (C), 118.1 (CH), 117.8 (CH), 35.4 (C), 31.7 (3CH\(_3\)); MS (ESI): \(m/z\) = 253.1 (M+H\(^+\)). Spectroscopic data was compared with that previously reported.\(^\text{2}\)

9H-xanthen-9-one (42): Following the general procedure (IV), 42 was prepared from aldimine 39 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). White solid\(^\text{24}\) (53 mg, 54% yield); m.p.: 172-174 °C (lit.\(^\text{24}\) m.p. 176-177 °C); IR (KBr): \(\nu_{\text{max}}\) 2920, 1655, 1458 cm\(^{-1}\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.30 (d, \(J = 7.9\) Hz, 2H), 7.69-7.64 (m, 2H), 7.42 (d, \(J = 8.4\) Hz, 2H), 7.31 (t, \(J = 7.2\) Hz, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 177.2 (C), 156.5 (C), 154.9 (C), 147.6 (C), 134.8 (CH), 133.5 (CH), 127.4 (CH), 123.7 (CH), 122.7 (CH), 122.0 (C), 121.3 (C), 118.1 (CH), 117.8 (CH), 35.4 (C), 31.7 (3CH\(_3\)); MS (ESI): \(m/z\) = 197.1 (M+H\(^+\)). Spectroscopic data was identical with that previously reported.\(^\text{24}\)
General procedure (V) for synthesis of phenanthridines

Aldimine (0.25 mmol) was dissolved in DCE (1 ml) and added in a mixture of PhI(OAc)$_2$ (0.375 mmol) and BF$_3$·OEt$_2$ (0.375 mmol) in DCE (3 ml). The resulting reaction mixture was stirred at room temperature for 5 min and then was refluxed for 30 h at 80 °C and then cooled to room temperature. Diluted with H$_2$O and extracted with diethyl ether (2 x 15 mL). The organic layers were combined, dried over Na$_2$SO$_4$, filtered, and the solvent removed under reduced pressure to afford the residue, which was purified by column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexanes as the eluent to provide the desired product.

8-chloro-6-phenylphenanthridine (49): Following the general procedure (V), 49 was prepared from aldimine 46 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). White solid (57 mg, 58% yield); m.p.: 143-145 °C; IR (Neat): 3062, 2990, 2927, 1606, 1510, 1495, 1466, 1455, 1354, 1250, 1235, 1170, 1032, 830, 777, 735, 726 cm$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.55 (d, $J$ = 7.7 Hz, 1H), 8.51 (d, $J$ = 7.7 Hz, 1H), 8.33 (d, $J$ = 7.3 Hz, 1H), 7.88 (s, 1H), 7.66-7.58 (m, 5H), 7.56-7.54 (m, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 160.1 (C), 144.2 (C), 139.9 (C), 135.3 (C), 132.6 (C), 131.6 (CH), 130.8 (CH), 129.5 (CH), 128.9 (2CH), 128.7 (2CH), 128.7 (CH), 127.9 (CH), 127.3 (CH), 125.7 (C), 124.2 (C), 122.2 (CH), 121.6 (CH); MS (ESI): $m/z$ = 290.1 (M+H)$^+$; HRMS (ESI) calculated for C$_{20}$H$_{12}$ClN: 289.0658, found: 290.0655 (M+H)$^+$.

8-methyl-6-phenylphenanthridine (50): Following the general procedure (V), 50 was prepared from aldimine 47 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). Yellow oil (56 mg, 57% yield); IR (Neat): $\nu_{	ext{max}}$ 3060, 2920, 1580, 1562, 1460, 1365, 1270, 766, 733, 703 cm$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.58 (d, $J$ = 8.2 Hz, 1H), 8.48 (d, $J$ = 7.8 Hz, 1H), 8.23 (d, $J$ = 7.8 Hz, 1H), 7.87 (s, 1H), 7.75-7.65 (m, 5H), 7.59-7.52 (m, 3H), 2.51 (s, 3H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 161.3 (C), 143.8 (C), 137.1 (C), 132.3 (C), 132.6 (C), 131.6 (CH), 130.8 (CH), 128.4 (2CH), 128.2 (CH), 127.2 (CH), 125.3 (C), 124.0 (C), 122.0 (CH), 121.5 (CH), 21.7 (CH$_3$); MS (ESI): $m/z$ = 270.1 (M+H)$^+$; HRMS (ESI) calculated for C$_{20}$H$_{15}$N: 269.1204, found: 270.1206 (M+H)$^+$.

6-phenylphenanthridine (51): Following the general procedure (V), 51 was prepared from aldimine 48 and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). White solid (49 mg, 48% yield); m.p.: 105-106 °C (lit. 109 °C); IR (KBr): $\nu_{\text{max}}$ 3058, 2920, 2851, 1560, 1482, 1458, 1444, 1310, 1300, 1288, 1135, 1073, 1029, 956, 784, 753, 727, 701, 672 cm$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.64 (d, $J$ = 8.4 Hz, 1H), 8.55 (d, $J$ = 8.4 Hz, 1H), 8.28 (d, $J$ = 7.7 Hz, 1H), 8.11 (d, $J$ = 8.1 Hz, 1H), 7.86-7.56 (m, 9H); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 161.2 (C), 143.7 (C), 139.8 (C), 133.3 (C), 130.5 (CH), 130.2 (CH), 129.7 (2CH), 128.8 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 126.7 (CH), 125.2 (C), 123.6 (C), 122.1 (CH), 121.9 (CH); MS (ESI): $m/z$ = 256.1 (M+H)$^+$; HRMS (ESI) calculated for C$_{18}$H$_{17}$N: 255.1048, found: 256.1044 (M+H)$^+$.

Spectroscopic data was compared with that previously reported.25
References:

Copies of $^1$H-NMR and $^{13}$C-NMR: